

Laboratory-scale pilot of enzyme-catalyzed CO₂ sequestration with produced waters as cation source

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Introduction

Our biomimetic approach to CO₂ sequestration has been described in previous publications. (See for example, references 1-3.) The aim is to sequester CO₂ in carbonate form, which offers several advantages. In particular, this offers a very long-term sequestration option, with low associated risks. Problems with licensing of disposal sites are not expected, and long-term monitoring is unlikely to be necessary.

The goal is to incorporate CO₂ into calcium carbonate via an aqueous process at mild pH values, and ambient or near-ambient temperature and pressure. If concentrations of Ca²⁺ and CO₃²⁻ ions in aqueous solution exceed the solubility limit, CaCO₃ can be precipitated. In order to incorporate CO₂ into CO₃²⁻ ions under these conditions, we must first form HCO₃⁻ ions. Hydration of CO₂ is the rate-limiting step in the reaction sequence. CO₂ fixation as carbonate is potentially viable if we can speed up this reaction. The biological catalyst, carbonic anhydrase, accelerates the reversible hydration of CO₂, and thus the use of this enzyme forms the basis of our approach.

Cation sources for carbonate formation will be location specific. Possible sources include seawater and brines, such as:

- Produced waters from oil and gas production.
- Waste streams from various industrial processes.
- Waste brines from desalination.

The use of waste streams offers the possibility of adding value to an existing waste product. Produced waters are our present focus. These brines from oil and gas production are produced in large quantities in areas such as the Permian Basin, where they are already being produced, transported, & reinjected. TDS (total dissolved solids) and cation concentrations vary from reservoir to reservoir. There is some usage of produced waters in water flooding for postsecondary production, but mostly they constitute a waste product, ~ 90 % of which is reinjected for disposal in the Permian Basin (moved by truck or pipeline). Can we add value to this waste product?

Bench-scale experiments

Representative compositions of produced waters, with both low and high TDS (total dissolved solids) values from the Permian and San Juan Basins, were selected to exemplify both high and low concentrations of Ca^{2+} and Mg^{2+} ions. The results presented here are for brines with compositions (Table 1) containing low concentrations of Ca^{2+} and Mg^{2+} (4,5). Data for brines with high concentrations of Ca^{2+} and Mg^{2+} should appear in reference (6).

mg/L	Na^+	Ca^{2+}	Mg^{2+}	K^+	Cl^-	SO_4^{2-}	HCO_3^-	TDS	$\text{Ca}^{2+}:\text{Mg}^{2+}$
Permian Basin	788	304	13	42	1040	1000	134	3321	14:1
San Juan	6622	179	33	53	8800	1225	1671	17735	3.3:1

Table 1. Compositions of produced waters with low concentrations of Ca^{2+} and Mg^{2+} ions.

Equal proportions of CO_2 - saturated water and synthetic produced water were mixed together with 0.2 ml 3.3mM BCA (bovine carbonic anhydrase). Tris buffer solution was added to give the desired pH. Time to onset of precipitation (from adjustment of pH of solution) was determined, in the presence of BCA and in control solutions (without BCA). The results are shown in Table 2.

		Precipitation time (sec.)	pH value
Permian Basin	With BCA (0.031mM)	231	8.71
	No BCA	369	8.70
San Juan Basin	With BCA (0.031mM)	No precipitation	8.57
	No BCA	No precipitation	8.61

Table 2. Precipitation from synthetic produced water with low concentrations of Ca^{2+} and Mg^{2+} ions.

No precipitation was observed from the simulated San Juan Basin brine, which contained the lower Ca^{2+} content, and also proportionately more Mg^{2+} ions. Since the solubility of calcium carbonate decreases with increasing temperature, and there is waste heat available at a power plant, the effects of modest heating on precipitation were investigated. It was found that precipitation occurred when the temperature was increased to $\sim 55^\circ\text{C}$. The results are shown in Table 3. Precipitation was also more rapid from the simulated Permian Basin brine.

	Permian Basin			San Juan Basin		
			With BCA (0.031mM)	No BCA	With BCA (0.031mM)	No BCA
Time (sec.)			47	57	110	114
pH value			8.70	8.70	8.69	8.71

Table 3. Effect of temperature on precipitation time.

In order to determine the amount of carbon sequestered in a single precipitation cycle, and its relation to the concentrations of Ca^{2+} and Mg^{2+} ions, ionic concentrations were determined before and after precipitation. The results are shown in Table 4. There was little if any change in Mg^{2+} concentration, but the initial concentration in these low-TDS brines was very low and so the driving force for MgCO_3 was lacking.

mg/L			Ca^{2+}	Mg^{2+}	CO_3^{2-}	HCO_3^-
Permian Basin		Before precipitation	143	6	29	467
		After precipitation	24	6	11	262
San Juan Basin		Before precipitation	84	16	75	804
		After precipitation	5.1	14	38	750

Table 4. Ionic concentrations before and after precipitation.

CO_2 sequestration efficiency was estimated as percent change in total amount of inorganic carbon (IC) in solution after carbonate precipitation. These results, together with percentage change in Ca^{2+} concentrations, are shown in Table 5.

mg/L	Permian Basin	San Juan Basin
IC before precipitation	95.6	209
IC after precipitation	43.5	181.9
Efficiency	54%	13%
Decrease in Ca^{2+}	83%	94%

Table 5. Sequestration efficiency for synthetic produced water with low concentrations of Ca^{2+} and Mg^{2+} ions.

The factor that limits the sequestration efficiency in low-TDS brines such as these is seen to be the Ca^{2+} ion concentration, with very high percentages of those ions being precipitated.

Parallel experiments are also in progress with brines corresponding to representative high-TDS compositions found in both the Permian Basin and the San Juan Basin. These results should appear in reference (6), along with estimates of sequestration capacity for the two basins based on these results. In this context, sources and volumes of produced waters for both the Permian and San Juan Basins have been ascertained (see Figure 1), as well as chemical compositions, based on data in references (4) and (5).

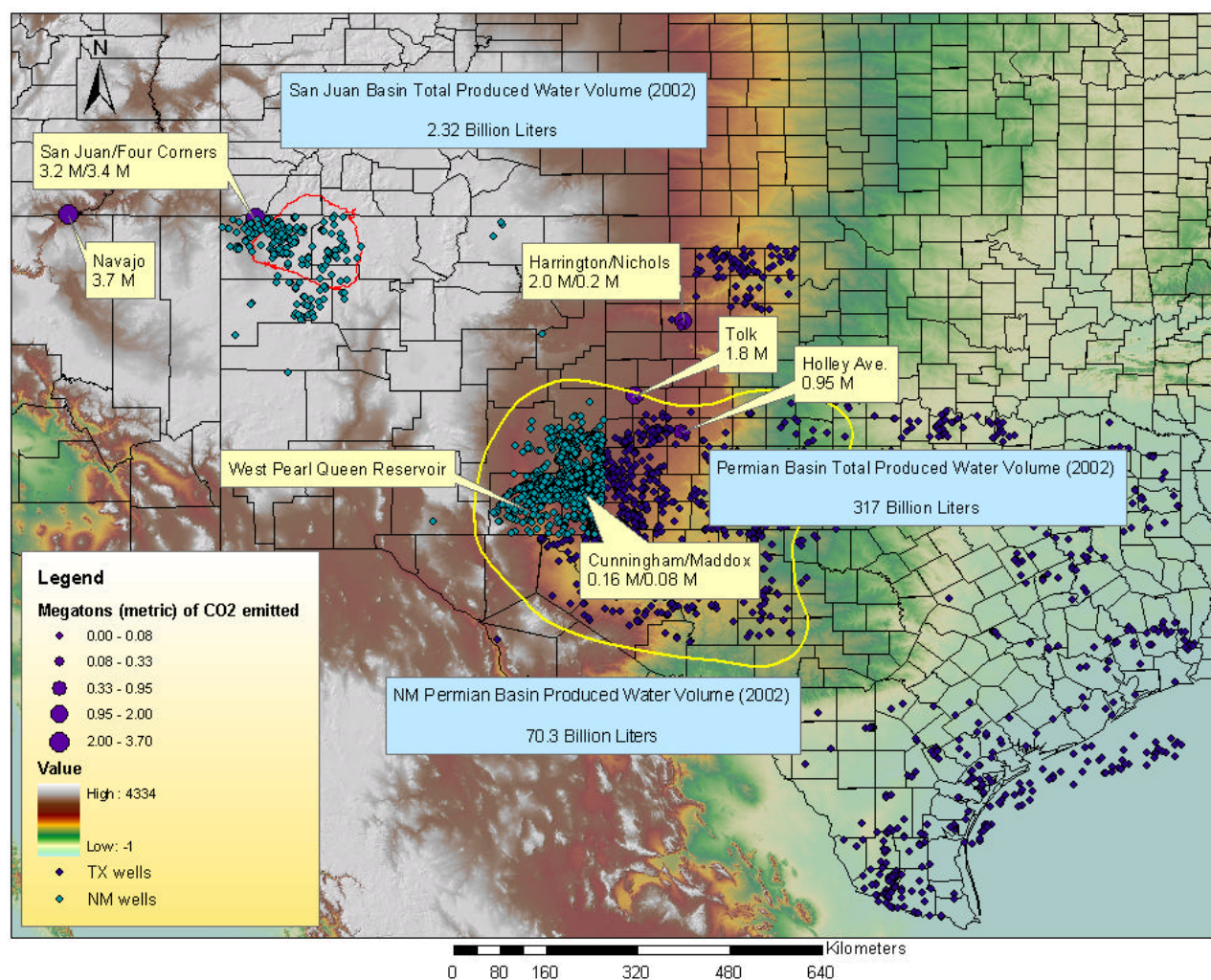


Figure 1. Sources and volumes of produced waters from the San Juan Basin and Permian Basin.

Laboratory-scale experiments

Laboratory-scale experiments have been conducted with much larger volumes of fluid. For these experiments, CO₂ - saturated water was pH adjusted with Tris buffer (to values in the range approximately 8.55 to 8.7), and then immediately flowed through a reactor containing BCA immobilized in chitosan-alginate beads, and combined with a similar volume of synthetic brine. Beads were prepared from 2% w/v (weight per volume) alginic acid in deionized water, and then added to 0.2M CaCl₂ solution (crosslinking agent) with 2% w/v chitosan (for more details on enzyme immobilization see reference 2).

The inflow rates used were ~1.1L/min for the CO₂ - saturated solution, 0.15L/min for a 1M Tris buffer solution, and ~1.0L/min for the produced water. Initial results are shown in Table 6.

		Time (sec.)	pH value
West Pearl Queen Reservoir	With BCA	252	8.63
	No BCA	303	8.71
San Juan Basin	With BCA	7	8.58
	No BCA	122	8.65

Table 6. Laboratory-scale precipitation from synthetic produced water with high concentrations of Ca²⁺ and Mg²⁺ ions.

The results for the high-TDS San Juan Basin brine are very good. Precipitation times are slower for the West Pearl Queen (Permian Basin) brine, which is believed to be the result of a much lower Ca²⁺:Mg²⁺ ratio. Experiments are in progress, to evaluate whether modest heating would also provide a feasible means of accelerating precipitation from brines of this type.

Summary

The viability of produced waters as a cation source has been demonstrated at both bench scale and laboratory scale. The following parameters have been identified, which influence sequestration rate and efficiency in the pH range ~ 8.5:

- Carbonic anhydrase
- Total inorganic carbon
- Calcium ion concentration
- Ratio of Ca²⁺: Mg²⁺ concentrations
- Decrease in supersaturation on precipitation
- Temperature

Acknowledgments

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